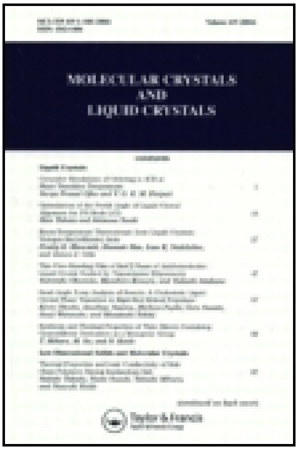

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Photochromic Protein Substrates

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A water-soluble spirooxazine may be successfully applied directly as dye to produce photochromic silk fabric. Molecular modelling, using the CAChe system, provides a good prediction of its photochromic properties. The dyed fabric shows good colour build-up under UV irradiation and reverts slowly to the original colour when the UV source is removed. It is observed that wet fabric shows better photochromic performance than after drying.

Keywords: photochromism; spirooxazine; textile dyeing; water-soluble

1. INTRODUCTION

Photochromic dyes are of considerable interest because of their functional applications, which include ophthalmics, security printing and optical data storage [1]. They also have the potential to generate dynamic colour change when applied to substrates such as textiles and leather. In this context, as fashion and effect materials, they offer exciting but as yet largely unexploited possibilities. We have carried out an extensive investigation into the design, using molecular

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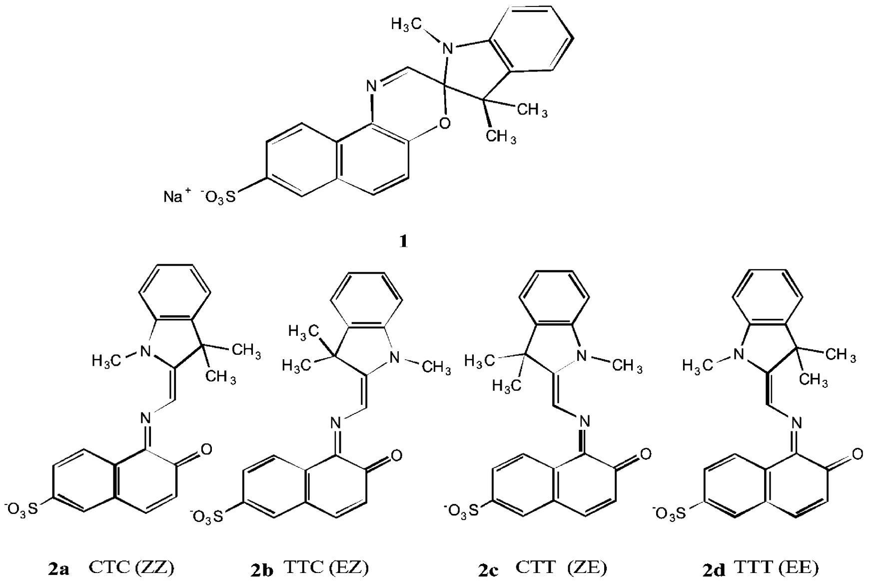

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2a CTC (ZZ) 2b TTC (EZ) 2c CTT (ZE) 2d TTT (EE)

FIGURE 1 Closed and transoid photomerocyanine forms of water-soluble spirooxazine (**1**).

modelling, synthesis and application performance of a series of water-soluble spirooxazine-based photochromic dyes specifically prepared for their suitability for direct application to protein substrates (patent application filed). The dyed substrates undergo change from colourless (or weakly coloured) to coloured (especially purple, blue and green) following exposure to sunlight or UV irradiation. The photochromic substrates, obtained after optimization of the application technology, show technical performance suitable for the production of fashionable materials, such as the leather footwear and accessories, apparel and furnishings. This paper focuses selectively on a study carried out on silk fabric with one example of a water-soluble spirooxazine photochromic dye.

2. RESULTS AND DISCUSSION

Spirooxazines show photochromic colour change when exposed to UV irradiation [1,2]. We have synthesised spirooxazine **1**, which is water-soluble due to the presence of the sulphonate group, in good yield and purity from the reaction of sodium 1-nitroso-2-naphthol-6-sulphonate with Fischer's base. There are eight possible geometrical isomers of the transient photomerocyanines formed from spirooxazines. Due to steric constraints, the four cisoid isomers are likely to be highly unstable, so that the present investigation has focused on the four transoid isomers **2a–d** as shown in Figure 1. We have recently demonstrated the usefulness of the application of a range of molecular modelling methods available within the CAChe software package for the prediction of photochromic and spectral properties of spirooxazines [2]. The results of calculations carried out on the anion of compound **1** and its potential photomerocyanines **2a–2d** using molecular numbers and semi-empirical methods are given in Table 1. The final energy (after MM2 minimisation) of **1** is lower than those of the four transoid photomerocyanine isomers and this is true also of heats of formation calculated using the semi-empirical methods AM1 and PM5, results which are consistent with expected photochromic behaviour. Compound **1** is indeed photochromic producing a blue colour on irradiation. The MM2 results predict that isomer **2b** is likely to be the most stable form. This is consistent with previous studies on the parent spirooxazine and is as expected since the sulphonate group is unlikely to influence significantly the steric constraints which determine the relative stabilities of the isomers [2]. Silk fabric, dyed with compound **1**at a level of 2% (on weight of fabric) shows a change from its original natural pale yellowish colour to a green colour (due to superimposition of the blue colour of the photomerocyanine) under UV irradiation (low-pressure mercury vapour discharge lamp, 20W, maximum wavelength 370 nm). The colour build up was assessed quantitatively from reflectance measurements converted to L^*, a^* and b^* values using the CIELAB system as illustrated in Figure 2(a)–(c). The colour build-up is characterized by a decrease in lightness (L^*), an increase in greenness ($-a^*$) and in blueness ($-b^*$). Figure 3 (a)–(c) illustrate how the fabric reverts to its original colour with time. In common with our observations on other substrates treated with these

TABLE 1 Calculated Energies from Molecular Modeling

Structure	Final energy (E_{MM2}) (kcal. mol^{-1})	Heat of formation (kcal. mol^{-1}) E_{AM1}	E_{AM1} (in water)	E_{PM5}	E_{PM5} (in water)
1	–3.54	−78.36	−184.66	−142.9	−260.2
2a	0.96	−75.02	−181.85	−127.9	−254.6
2b	−1.97	−72.27	−178.74	−123.3	−251.1
2c	4.12	−72.22	−180.07	−129.0	−254.1
2d	1.97	−72.14	−176.86	−127.8	−254.2

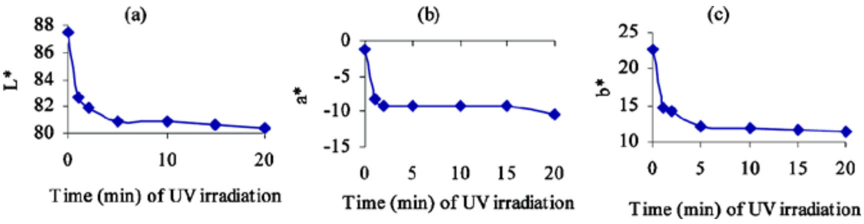

FIGURE 2 (a)–(c) The variation of L*, a* and b* values of silk fabric dyed with spirooxazine (**1**) with time of UV exposure.

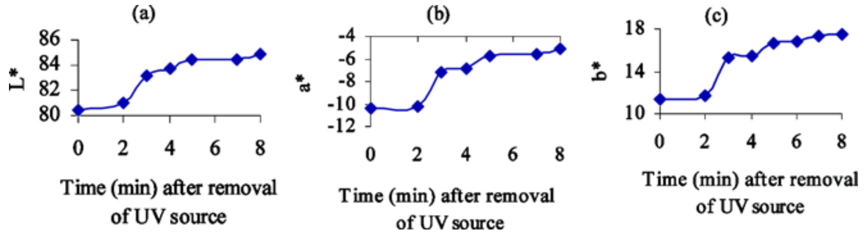

FIGURE 3 (a)–(c) Decoloration of dyed silk fabric with time after removal of the UV source.

dyes, the UV-induced colour change on silk (Table 2) is more pronounced when wet than after drying. A reason may be that the dye molecules have high mobility on wet fabric which facilitates the photochromic conversion, but this mobility is restricted after drying. An alternative explanation is suggested by AM1 and, more convincingly, PM5 results (Table 1). The energy difference between the closed form (**1**) calculated by PM5 and the photomerocyanines is significantly higher than when calculated using a semi-empirical minimisation technique that attempts to take account of water solvation [3]. The dyed silk shows reasonable technical performance, such as wash fastness and photostability. Significant colour build up under UV

TABLE 2 Colour Build up in Dry and Wet State of the Dyed Silk Fabric

State of the sample	Colour before UV irradiation			Colour after UV irradiation for 2 min		
	L*	a*	b*	L*	a*	b*
Dry	87.34	−1.0	22.3	80.8	−10.13	11.90
Wet	82.95	−0.9	32.5	65.2	−22.76	−0.45

irradiation remains after a standard wash fastness test [4]. The photochromic effect on dyed silk reduces on exposure in a Xenotest accelerated fading instrument, although significant photochromic colour change is observed for up to 90 hours exposure (dry) and 300 hours (wet).

3. CONCLUSION

The calculated final energy (MM2) and heats of formation (AM1 and PM5) of a water-soluble spirooxazine (**1**) are lower than those calculated for the possible photomerocyanine isomers, consistent with the observed photochromic behaviour. The dye may be applied successfully to produce a silk fabric which changes colour under UV irradiation. The wet dyed silk fabric undergoes stronger colour build up than in the dry state with similar UV irradiation. Results from our more extensive investigation of a range of novel water-soluble photochromic dyes and their application performance on a variety of textile and leather substrates will form the basis of future publications.

REFERENCES

[1] Crano, C. J. C. & Guglielmetti, R. J. (Eds.), (1999). *Organic Photochromic and Thermochromic Compounds*, Kluwer Academic/Plenum Publishers: New York, Vol. 1 & 2.

[2] Christie, R. M., Chi L. J., Spark, R. A., Morgan, K. M., Boyd, A. S. F., & Lycka, A. (2004). *J. Photochem. Photobiol. A.: Chem., 169*, 37–45.

[3] Toshio, H., Okada Y., & Morita, Z. (2003). *Dyes and Pigments, 59*, 25–41.

[4] Standard Methods for the Determination of the Colour Fastness of Textiles and Leather, Fifth edition, 1990, The Society of Dyers and Colourists, Perkin House, Bradford, BD1 2JB, UK.